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AFRPL-TR-68-96

(Unclassified Title)

THERMAL STABILITY AND AGING STUDIES ON SELECTED NF COMPOUNDS

Ivan C. Smith
John W. Nebgen
Thomas W. Lapp
Midwest Research Institute

Contract No. FO4611-68-C-0011

May 1968

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Research and Technology Division
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FOREWORD

This program is being conducted at Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under the general supervision of Mr. R. L. Hughes, Director, Chemistry Division. Dr. A. D. McElroy, Head of the Inorganic Chemistry Section, is the program supervisor. Dr. I. C. Smith, Principal Chemist, is project leader. Personnel contributing to the program are Drs. J. W. Nebgen, T. W. Lapp, W. V. Best, and Mr. N. Stitch. The program is being monitored by 1/Lt Raymond E. Foscante, RPCS, Edwards Air Force Base.

The research covered by this report is being conducted under Contract No. F04611-68-C-0011 (Midwest Research Institute Project No. 3100-C) and covers the period 1 July 1967 - 1 May 1968.

This report covers only the work related to P-BEP stability and compatibility. Reports will be issued in the future on other phases of this program.

Publication of this report does not constitute Air Force approval of the report's findings and conclusions. It is published only for the exchange and stimulation of ideas.

This report has been reviewed and approved.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division

ABSTRACT

(C) The stability of P-BEP and its compatibility with HAP, HP-2, AP, and curing agents have been studied.

(C) P-BEP slowly evolves HF, HCN, and HNF_2 at or near 25°C. Although the quantities of these gases evolved are small, they are sufficient to have an adverse effect on curing reactions, and will likely create problems in long-term storage.

(C) Both HAP and HP-2 promote decomposition and oxidative degradation of P-BEP. HP-2 appears to be too reactive to be formulated into a propellant which utilizes a P-BEP binder. The prospects of obtaining a storable propellant from the HAP/P-BEP system appears to be marginal. Of the oxidizers studied, only AP seems to be compatible with P-BEP.

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I.

INTRODUCTION

(U) Midwest Research Institute is conducting a research program under Air Force Contract No. F04611-68-C-0011 to determine the stability and compatibility of propellant ingredients. These studies are designed to define propellant-processing limitations, and to identify problems which may develop during storage and aging of propellants formulated from these ingredients.

(C) This report covers work thus far completed on the stability of P-BEP and on its compatibility with ammonium perchlorate, hydroxylammonium perchlorate, hydrazinium diperchlorate, an isocyanate (DDI), and an epoxy (ERLA-4221) curing agent.

(U) Experimental techniques employed on this program include: infrared, nuclear magnetic-resonance and electron spin-resonance spectroscopy, mass spectrometry and gas chromatography.

II.

BACKGROUND

(C) P-BEP is prepared by Shell Development Company by direct addition of N_2F_4 to poly(2,3-epoxypropene). The average structure of the prepolymer as proposed by Shell[1] is:

(c)

$$CH_2-O-\left[CH_2-\underset{NF_2}{\overset{CH_2-NF_2}{\underset{|}{\overset{|}{C}}}}-O\right]_m-CH_2-\underset{}{\overset{CH_2OCH_3}{\underset{|}{CH}}}-OH$$

$$CH-C-\left[CH_2-\underset{NF_2}{\overset{CH_2-NF_2}{\underset{|}{\overset{|}{C}}}}-O\right]_n-R$$

$$CH_2-O-\left[CH_2-\underset{NF_2}{\overset{CH_2-NF_2}{\underset{|}{\overset{|}{C}}}}-O\right]_o-CH_2\underset{CH_2OCH_3}{\overset{}{CHOH}}$$
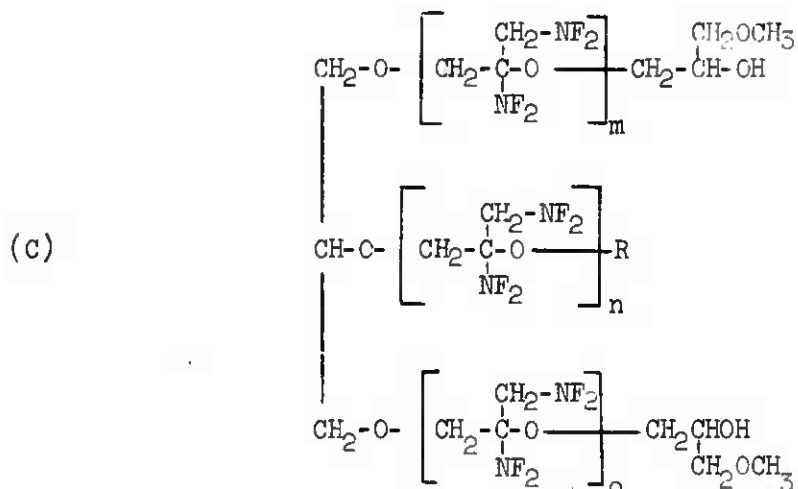
$m + n + o = 26$ to 30

R $\qquad$ = nonfunctional termination

P-BEP is a highly viscous liquid with a typical number average molecular weight of 3,300 to 4,400. Fractionation of the polymer at UTC[2] showed that approximately 10 percent of the polymer has a molecular weight of 5,500 or greater and 30 percent has a molecular weight below 2,800. The lowest molecular weight fraction (MW~1,200) isolated was reported to be much less stable than the higher molecular weight fractions.

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[1] Hunter, L., and E. E. Ryder, Shell Development Company, Final Technical Report on Air Force Contract No. AF 04(611)-11412, Feb. 1967.

[2] Ives, E. K., R. M. Kumagai and R. P. Moen, United Technology Center, Quarterly Report AFRPL-TR-68-6, Air Force Contract No. FO 4611-67-C-0039, December 1967.

(C) Studies on the slow thermal decomposition of P-BEP performed at Dow Chemical Company[3] on Shell Lot No. 9557-82, (MW = 3670) gave HF, HCN, N_2, CO_2 and N_2F_4 as the principal gaseous decomposition products at 150° and 160°C, with minor quantities of NF_3, N_2F_2, HNF_2 and N_2O. Mass spectrometric analysis of the solvent from "as-received" P-BEP indicated the presence of n-pentane, 2-methylbutane, acetone, pentene and hexane as contaminants. Total gas-evolution measurements showed approximately 220 cc. of gas evolved per gram of P-BEP in 4.5 hr. at 150°C. A 20 percent weight loss of P-BEP occurred at this temperature in the same time period.

(U) Thermal stability studies on neat P-BEP (lot 9165-107) performed at UTC[4] showed that the polymer contained 0.5 to 2 percent methylene chloride. At 45 and 60°C, solvent loss, which was diffusion-controlled, continued for approximately 200 hr. The weight losses of neat P-BEP (containing 0.5 to 2 percent methylene chloride) were 0.25 to 0.30 percent in 1,000 hr. at ambient temperature, 1.9 percent in 1,000 hr. at 45°C, and 4.8 percent in 1,000 hr. at 60°C. Part of the weight loss was attributed to solvent evaporation.

(C) Rapid pyrolysis studies have been performed on P-BEP at Lockheed Propulsion Company.[5] The procedure involves pyrolyzing the sample on a platinum ribbon located within 2 mm. of the ionizing electron beam in a Bendix time-of-flight, model 12-101, mass spectrometer. The heating rates commonly employed were in the range of hundreds of degrees per second. The initial ion fragments detected were $C_3H_4^+$, $C_2H_3O^+$, $C_2H_5O^+$ and $HCNF^+$. In their studies HF began to appear at about 60°C. More recent results on this contract were not available to the authors at the time this report was being prepared.

(C) The results of previous studies on the stability of P-BEP clearly indicate that a more definitive picture of the mode and rate of its decomposition is needed, particularly under conditions which would be employed in formulating a propellant using a P-BEP binder.

[3] Dow Chemical Co., Quarterly Tech. Report AFRPS-TR-67-197 on Air Force
    Contract No. AF 04(611)-11395, July 1967.
[4] Allen, P. L., E. K. Ives, and T. N. Scortia, United Technology Center
    Report No. AFRPL-TR-66-84, April 1966.
[5] Lockheed Propulsion Company, Technical Report No. AFRPL-TR-67-182,
    June 1967.

(C) Studies performed on this program were designed:

    (1) to determine the types of decomposition P-BEP undergoes at propellant processing temperatures;

    (2) to determine the rate of decomposition as a function of temperature; and

    (3) to determine, if possible, the temperatures at which the various modes of decomposition are initiated.

(C) In addition, the compatibility of P-BEP with AP and the energetic oxidizers HAP and HP-2 was investigated. These studies were designed to identify formulation problems which might develop in preparing propellants containing these energetic ingredients, and to obtain information on the storability of such propellants.

(C) Preliminary studies were also performed on the compatibility of P-BEP with the curing agents DDI and ERLA-4221.

III.

EXPERIMENTAL PROCEDURES

A. P-BEP Purification and Handling

(U) Two lots of P-BEP have been used in these studies. All of the early work was performed on Lot No. 9557-82, while more recent work has been with Lot No. 10001-168. Shell submitted the following data on these samples. Lot No. 9557-82 reported to have a number average molecular weight of 3,670 and a thermal stability of 4.6 cc. of gas liberated per gram of P-BEP per 100 hr. at 80°C. Sample No. 10001-168 had a number average molecular weight of 3,400 and a thermal stability of 5.2 cc. of gas liberated per gram of P-BEP per 100 hr. at 80°C. No difference in stability or compatibility was observed for the two samples in these studies.

(U) The P-BEP used on this program was shipped as a methylene chloride solution. Proton NMR spectra of the as-received material indicated that the solution contained hydrocarbon impurities. These impurities were identified in a Dow report[6] as n-pentane, 2-methylbutane, acetone, pentene and hexane. Since P-BEP was found to be relatively insoluble in Freon-11, all P-BEP used in these studies was purified by precipitating it from methylene chloride with Freon-11. Three successive precipitations were employed in this purification, which resulted in a loss of 10 to 15 weight percent of the P-BEP. It was recently reported by UTC that the low molecular weight fractions of the polymer are retained in Freon-11 solvent. Based on the weight loss observed and the molecular weight distribution reported by UTC,[2] this would indicate that the fraction removed would have molecular weights below 2,000. No evidence of hydrocarbon impurities could be detected by NMR in P-BEP purified by this procedure.

B. Oxidizer Handling

(U) Oxidizers used in these studies were ammonium perchlorate (AP), hydroxylammonium perchlorate (HAP) and hydrazinium diperchlorate (HP-2). The storage and handling of all of these oxidizers was performed in a dry box having a -80°C dew point.

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[6] Dow Chemical Company, Quarterly Technical Report No. AFRPL-TR-67-265 October 1967.

(U) AP was obtained from G. Frederick Smith Chemical Company. The HAP used in these studies was furnished by the Elkton Division of Thiokol Chemical Company. Analysis of this oxidizer sample at MRI indicated a purity of about 98 percent. The HP-2 was furnished by the Wasatch Division of Thiokol, and had a reported purity of 98.84 percent.

C. Experimental Techniques

(U) The low temperatures generally employed in these studies required the use of sensitive analytical techniques to detect and identify the reaction products resulting from the decomposition of P-BEP. No single experimental tool is available which would yield all the information needed to identify the types and quantities of gas-phase decomposition products evolved from P-BEP and the chemical changes which occur in the polymer. As a consequence, the combined capabilities of IR, NMR and ESR spectroscopy plus gas chromatography and mass spectrometry were employed on this study.

(U) Infrared spectroscopy was used to continually monitor the quantities of infrared active gaseous decomposition products liberated from P-BEP as a function of time and temperature. A 100-mg. sample of P-BEP was placed in a stainless steel sidearm attached to a 10 cm. Kel-F infrared cell fitted with silver chloride windows. The entire cell was passivated with chlorine trifluoride for 2 hr. at 8 psig before placing the P-BEP in the sidearm and the entire system was evacuated at 10^{-4} Torr for 2 hr. The sample was then heated with a small thermocouple-controlled brass block heater (Figure 1) thermally regulated by a "limtrol" thermal regulator which is sensitive to $\pm$ 1°C. A Beckmann model IR-12 infrared spectrophotometer scanned the spectral region 700-3,960 cm.$^{-1}$ continually every 55 min. (Figure 2). These scans were normally continued for 16 hr. After 16 hr. the gaseous decomposition products were analyzed by gas chromatography and mass spectrometry.

(C) Reasonably good measures of the quantities of residual methylene chloride, present in the sample, and of HCN, HF, N_2O, NF_3, and N_2F_4 liberated during the decomposition were obtained from infrared spectra. Gas chromatography yielded quantitative data on the N_2, O_2, CO, NO, CO_2 and N_2O content of the gaseous decomposition products. A portion of the gaseous decomposition products were retained for mass spectrometric analysis to supplement and confirm other methods of analyses.

(U) For longer-term studies, 100-mg. samples of P-BEP were placed in passivated stainless steel tubes, evacuated and immersed in constant temperature baths for the desired time intervals. When removed from the constant temperature baths, they were attached to the Kel-F infrared cells

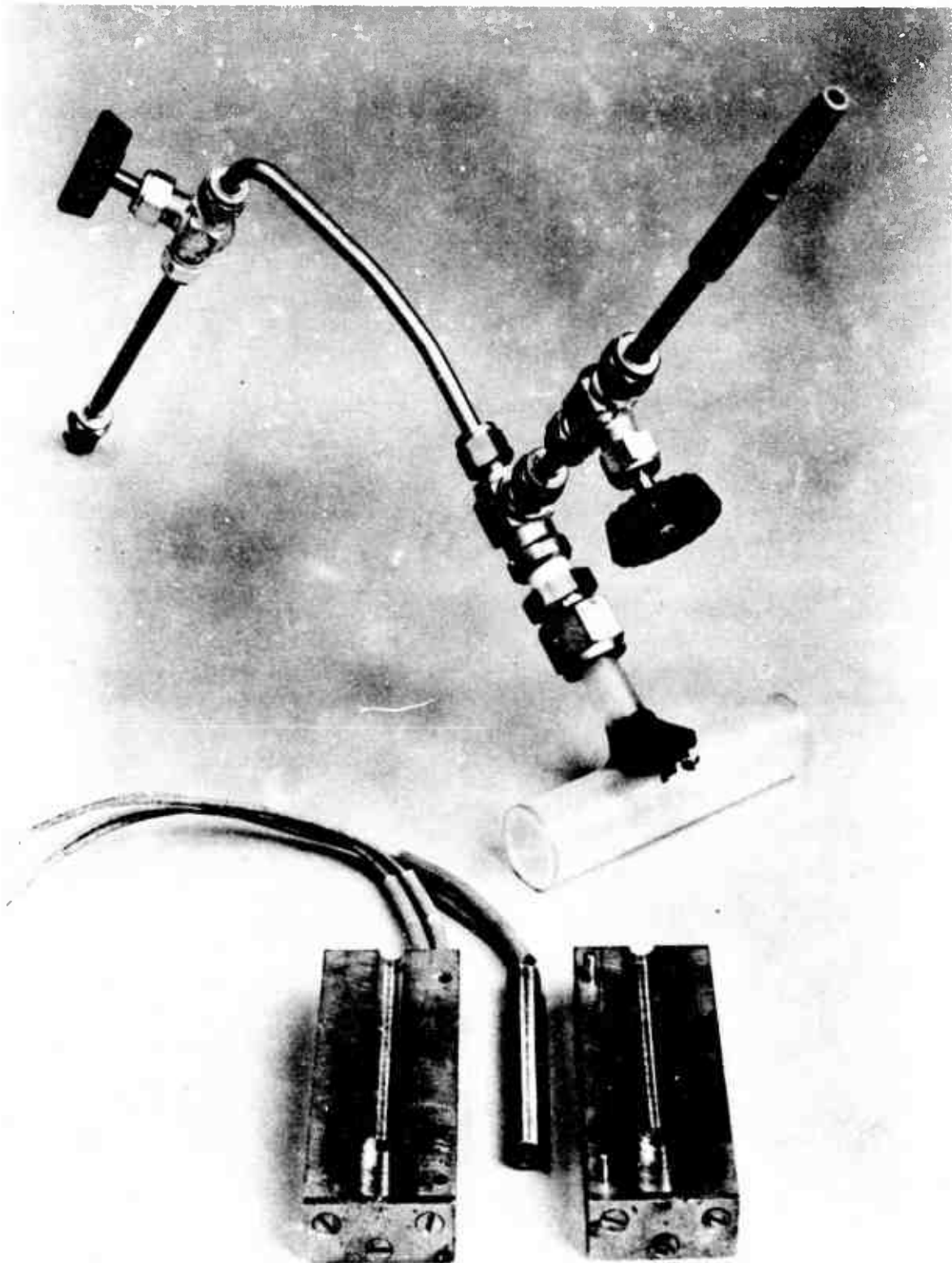Figure 1 - Thermocouple-Controlled Brass Block Heater

Figure 2 - Beckmann Model IR-12 Infrared Spectrophotometer

and the gaseous products analyzed by the procedures previously described. Temperatures employed for these studies were 25°, 40°, 55°, 70° and sometimes 85°C.

(U) Spectra of P-BEP polymer were obtained as a function of time and temperature on the Beckman IR-12 Spectrophotometer using a Limit VLT-2 variable temperature cell. Samples were mounted between two silver chloride discs inserted into the cell compartment, evacuated and heated.

(U) ESR spectra of neat P-BEP were obtained by means of a Varian Associates V-4502 ESR spectrometer to determine whether P-BEP contains residual paramagnetic species, or whether such species could be detected during its thermal decomposition. Evacuated P-BEP samples were placed in a variable temperature assembly and spectra obtained over the temperature range 25 to 175°C.

(U) NMR spectra were obtained on a Varian Model HA-100 NMR spectrometer equipped with a variable temperature accessory. Proton analyses were obtained with a Varian Associates A-60 NMR system.

(U) A Perkin-Elmer gas chromatograph equipped with a 12-ft. Porapak type Q, 1/4 in. column operated at -20°C was used to detect N_2, O_2, CO, NO, CO_2 and N_2O.

(U) Mass spectral analyses of the gaseous decomposition products were obtained with an Atlas Model CH4-B mass spectrometer equipped with an all metal inlet system. Nominal ionizing voltages of 70 ev. were used with an ionizing current of 35 μa. The inlet system was normally maintained at 60°C and the ion source at 250°C.

(U) The thermal dissociation of P-BEP polymer was studied using the direct inlet accessory of the mass spectrometer. This technique consists of placing a minute quantity of freshly purified P-BEP in a gold crucible. After placement in the direct inlet probe, the crucible is inserted directly into the mass spectrometer to a distance 1 mm. from the ion source. The temperature of the crucible can be externally controlled. Normally each sample was evacuated for approximately 15 - 20 min. at the ambient temperature within the mass spectrometer (~30°C). During this time period, a mass spectrum was obtained every 5 min. During the heating process, the temperature of the crucible was increased in approximately 10°C intervals with one mass spectrum being obtained shortly after the temperature was equilibrated. A second mass spectrum was recorded 5 min. after the first one.

(C) The compatibility of P-BEP with AP, HAP and HP-2 was also investigated utilizing infrared spectroscopy and gas chromatography. Approximately 50 mg. of the oxidizer was combined with 100 mg. of P-BEP for these studies.

IV.

EXPERIMENTAL RESULTS

A. P-BEP Stability

(U) 1. Mass spectrometry: The evolution of gaseous decomposition products from P-BEP was studied by mass spectrometry, infrared spectroscopy and gas chromatography. Chemical changes within the P-BEP polymer were investigated by infrared and ESR spectroscopy.

(U) The results of a brief study of the initial decomposition products observed from neat P-BEP utilizing the solid sampling (direct inlet) technique afforded many interesting insights into the mechanism of the thermal dissociation. A tabulation of the observed mass peaks resulting from the P-BEP degradation and the assigned ions is given below. The temperature range for the study was from ambient to 140°C.

TABLE I

PRINCIPAL ION PEAKS OBSERVED DURING P-BEP DEGRADATION (C)

m/e	ions	m/e	ions
20	HF^+	31	CF^+, CH_3O^+
26	CN^+	33	NF^+
27	HCN^+	43	$C_2H_3O^+$
28	N_2^+, CO^+, $C_2H_4^+$	44	CO_2^+, N_2O^+
29	CHO^+, $C_2H_5^+$	45	$C_2H_5O^+$
30	NO^+	52	NF_2^+
		53	HNF_2^+

(C) Other ions can be assigned to some of the m/e values; however, those shown represent the ions which are thought to be the major contributors to the particular mass value. In addition to the m/e values above, additional values were observed at m/e 47, 66, 82 and 101. These ions are thought to be arising from the fragmentation of Freon-11 which was used in the purification process. Dow Chemical Company.[6] has also studied the dissociation of P-BEP by the solid sampling technique. Their studies were conducted at 150°C, and the ion fragments were the same as observed in this study except for m/e 71 and 131. These fragments were not observed in the present study and m/e 85 (SiF_3^+) was not observed in appreciable quantities at temperatures

below 120°C. Figures 3 to 5 show the variation in peak intensity as a function of temperature for a number of the species resulting from the P-BEP decomposition. No correction could be made for a background contribution. In most cases, the initial peak intensity (at ambient temperature) is sufficiently small that it does not interfere with the interpretation of the observed curve.

(C) Hydrogen fluoride, the major species from the degradation, has been found to be present in P-BEP at room temperature. A mass spectrum obtained immediately after insertion of the sample probe shows an intense peak at m/e 20. This peak rapidly decreases in intensity as the sample is allowed to remain at the ambient temperature in the mass spectrometer and reaches a constant peak height of rather low intensity. With increasing temperature, the evolution of HF proceeds rather slowly up to approximately 70°C. In this region, the evolution becomes more pronounced and the rate increases with temperature up to 110°C. In the temperature region from 110-115°C, the production of HF increases very rapidly, and increasing the temperature from 115°C to 135°C results in an increase in the mass 20 peak from approximately 100 to 300 scale units.

(C) Hydrogen cyanide formation as a function of temperature parallels that of HF, although HCN is generated in smaller quantities. A mass spectrum obtained immediately after insertion of the probe does not show a large parent peak as is the case with HF, indicating that HCN is not present in the polymeric material as a dissolved gas. Hydrogen fluoride is formed at room temperature and is retained as a dissolved gas. This apparently is not the case with HCN. However, there is IR evidence that HCN is evolved at ambient temperature. Increasing the temperature from ambient to approximately 100°C results in a slow increase in HCN formation. Above this temperature the evolution of HCN becomes much more rapid but the increase is much less severe than in the case of HF. It is significant to note that the temperature range where HCN production begins to increase is the same temperature range where the evolution of HF becomes rapid.

(U) The production of CO_2, N_2O and possibly NO can be observed by a comparison of m/e 44 and m/e 30 values as a function of temperature. Both curves remain almost constant up to approximately 75°C where m/e 44 shows an increase in the production of either CO_2 or N_2O. The m/e 30 curve increases very slowly up to 90-100°C where the rate of evolution begins to increase. Both of these mass values were present immediately after insertion of the sample probe, with ion intensities greater than would be expected from air, indicating that these species may be present as dissolved gases in the P-BEP or are being slowly produced at room temperature.

11
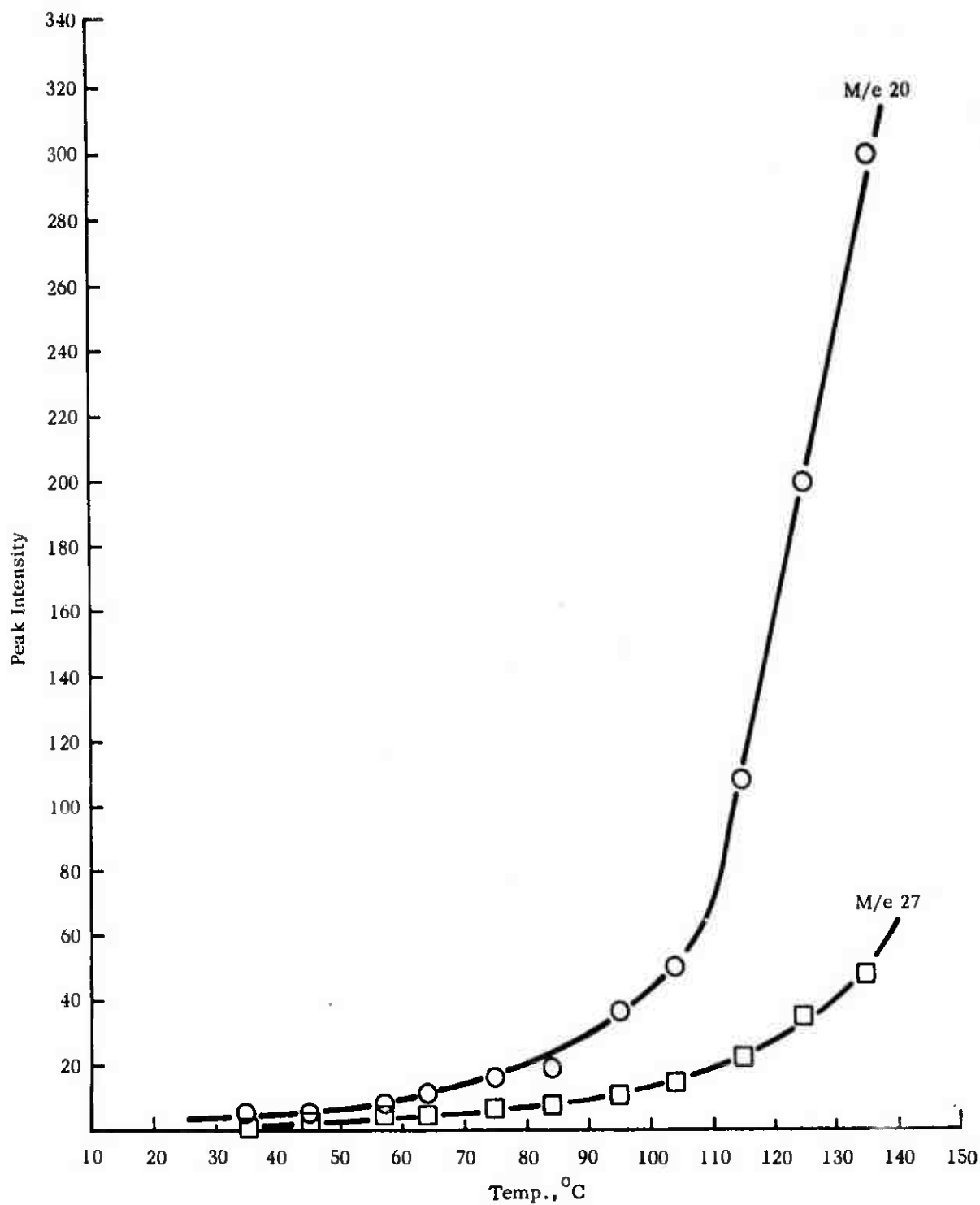
Figure 3 - Variation in Peak Intensity (arbitrary units) With
Temperature For m/e 20 and 27

12
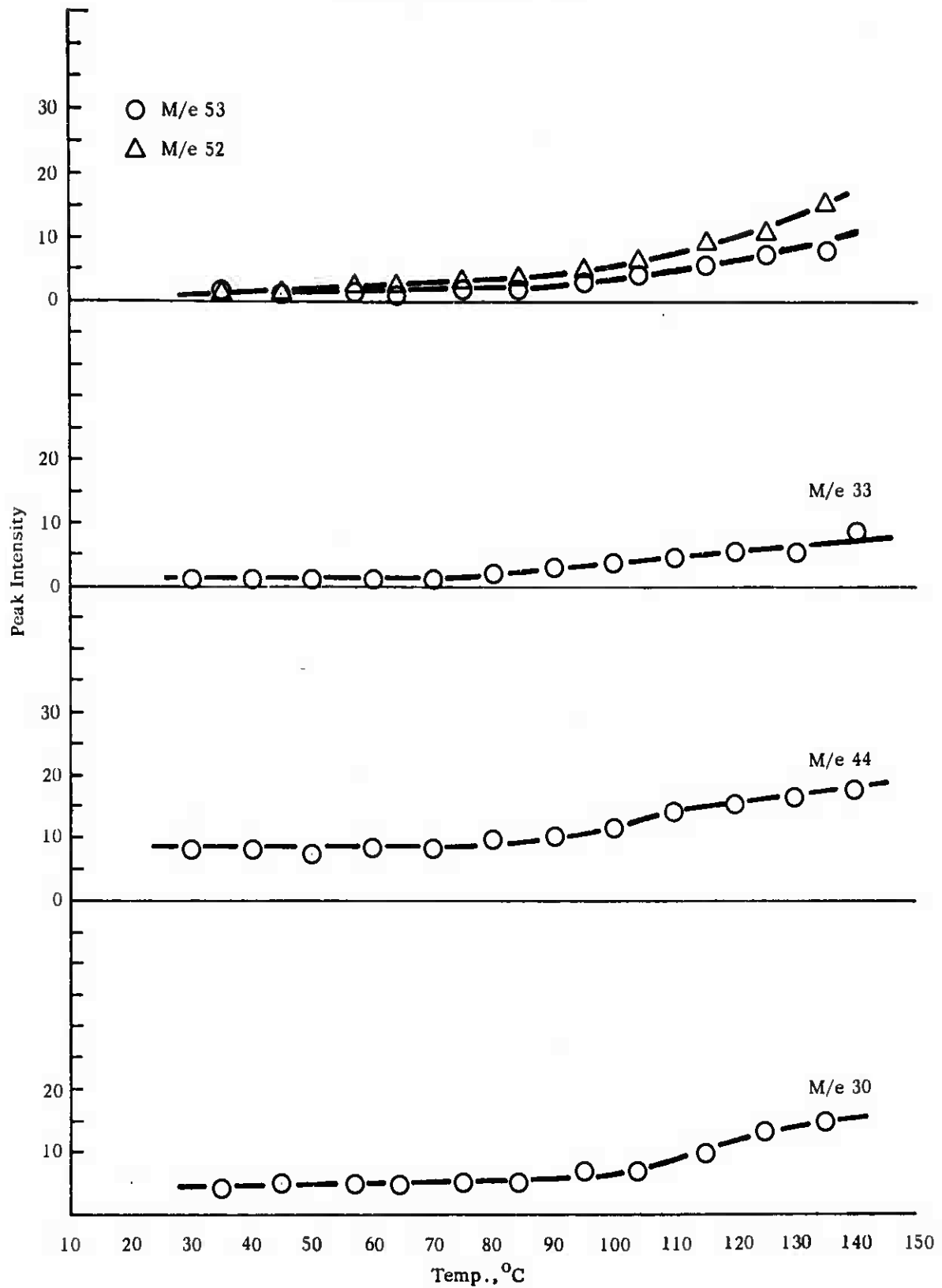
Figure 4 - Variation in Peak Intensity (arbitrary units) With Temperature

13
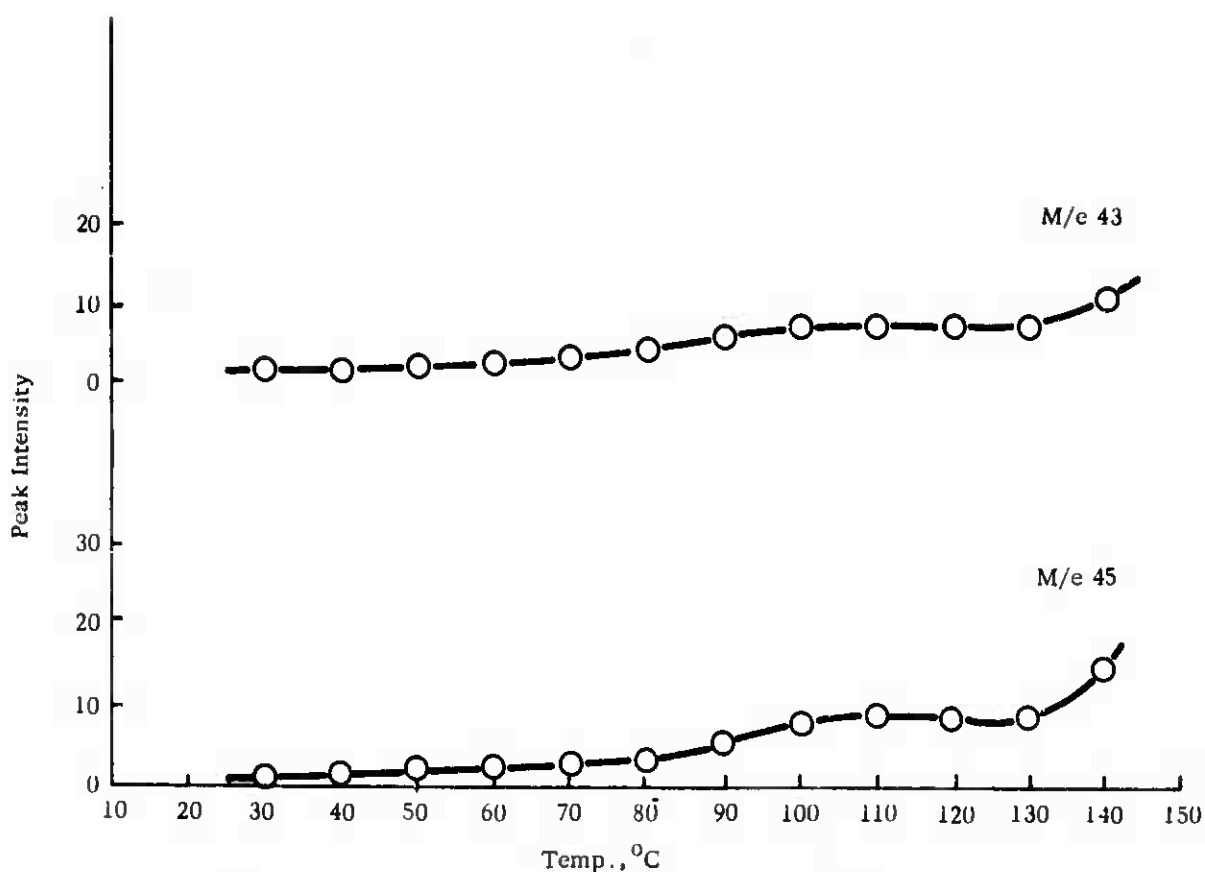
Figure 5 - Variation in Peak Intensity (arbitrary units) With
Temperature For m/e 43 and 45

(C) Evolution of difluoramine, as evidenced by the curve for m/e 53,
occurs very slowly up to 85°C. Above this temperature, the rate of pro-
duction becomes much more pronounced. The curves for m/e 33 and m/e 52
both remain essentially constant up to 75-80°C, at which point the rate
increases for both curves with the curve for m/e 53 increasing at a some-
what greater rate. The mass values 52 and 33 correspond to the NF_2^+ and
NF^+ ions, respectively, and are the principal ions produced in the mass
spectrum of tetrafluorohydrazine (N_2F_4). Nitrogen trifluoride (NF_3) also
shows large relative abundances at m/e 33 and 52, in addition to the par-
ent peak at m/e 71. In fact, the NF_2^+ ion is the largest peak in the
mass spectrum of NF_3, with the NF^+ ion having a relative abundance of
approximately 40. Dow[6]/ has reported that the mass 53 peak consists of
a doublet of equal intensity. The fragments observed at this mass value
correspond to HNF_2^+ and $HC_2N_2^+$.

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(U) Mass 45 is probably due to the $C_2H_5O^+$ ion and likely is formed as a result of the degradation of the terminal groups. The ion intensity increases very slowly up to 75-80°C, whereupon an acceleration of the rate is observed up to approximately 100°C. At this point, the rate appears to remain constant up to 130°C, and then increases much more rapidly at temperatures above 130°C.

(C) An interesting observation was made with the peaks at m/e 31 and 47. These two mass values correspond to CF^+ for the former and to a number of ions, including CCl^+, COF^+ and CH_2NF^+, for the latter. Originally it was thought that the ion fragments at these mass values resulted from the fragmentation of Freon-11 and indeed the intensity vs. temperature curves do show an increase from room temperature to a maximum at approximately 75°C and then a decrease. This corresponds directly to the curve obtained for m/e 101, the CCl_2F^+ fragment from the Freon. However, at approximately 110°C the ion intensity began to increase and showed a continual increase to 140°C. It is apparent that another process, resulting in the formation of ion fragments at m/e 47 and 31, is of importance at these higher temperatures. Such a process could involve the formation of the COF^+ and CF^+ ions.

(U) The various ions contributing to m/e 28 could not be studied due to the presence of an air leak. This difficulty is in the process of being corrected.

(C) A plot of log (ion intensity) as a function of $\frac{1}{T}$ for m/e 20 and m/e 27 is shown in Figure 6. The data for m/e 20 give a relatively straight line at lower temperatures which can be extrapolated to cross the temperature axis at approximately 5°C. However, the plot for m/e 27 does not produce a straight line relationship and apparently shows a complex situation at lower temperatures. Due to the measurement of ions of very low intensity, considerable error may be expected in the data at lower temperatures. The data indicate, however, that HCN is evolved at temperatures less than ambient and that HF is evolved at or slightly above 5°C.

(C) In general, the data show that P-BEP undergoes only slow degradation at temperatures lower than 70-80°C. Furthermore, HF begins to evolve at temperatures below ambient, HCN may be evolved at room temperature or slightly above and HNF_2 some 10-20°C above ambient temperature. At temperatures above 80°C, considerable dissociation commences and above 120-130°C the rate of decomposition is found to be quite rapid, as evidenced by the large relative increases in ion intensity.
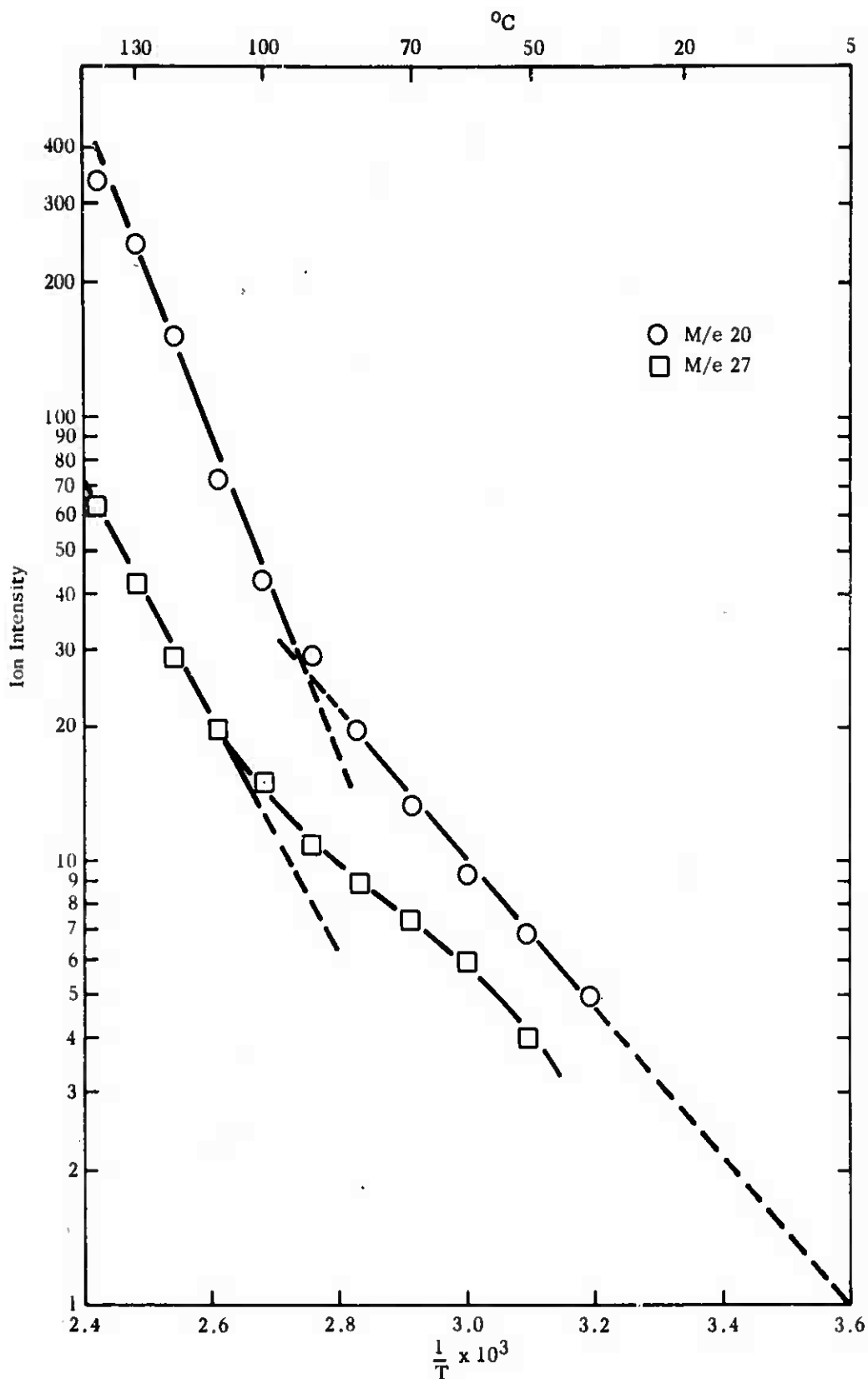
Figure 6 - Log (ion intensity) vs. 1/T (°K)
for m/e 20 and 27

(U) 2. _Infrared Studies_: Infrared spectroseopy has been used extensively in studying the stability of P-BEP. Most of the work has been concerned with P-BEP decomposition as a function of temperature for short term periods (16 hr.). In these studies, P-BEP was placed in a metal tube attached to a Kel-F infrared cell (Figure 1). The tube was heated to a constant temperature and the spectra were continuously recorded overnight.

(C) Products evolved from the heated P-BEP which were detected by IR were usually CH_2Cl_2, HF, HNF_2, HCN, N_2O and CO_2. The amounts of these materials reported in milliliters of standard gas per gram of P-BEP are presented in Table II. The studies were conducted in different metal tubes. From Table II, it appears that the smallest quantities of gaseous products are evolved in a copper reactor. However, extensive reaction of P-BEP and copper was noted; thus we believe that the volatiles probably reacted out before they could be detected. Monel, nickel, and stainless steel were then used. P-BEP did not appear to react with any of these. After preliminary studies in these metals, stainless steel was chosen for use in the detailed work. This choice was dictated on the grounds of convenience, since all of the metals except copper appeared to be compatible with P-BEP.

(U) Difficulty was experienced in getting reproducible results in the infrared studies. Runs made with the same quantities of P-BEP at the same temperature and monitored over the same time periods gave a scatter of points. However, the effect of temperature and time is critical enough that the data spread at a particular temperature were not sufficient to affect the conclusions drawn from these studies. The variance in data gathered from identical runs appears to depend to a very large extent upon the quantities of residual CH_2Cl_2 in the P-BEP itself.

(U) The overnight runs generated volatile products at temperatures between 50°C and 120°C. In these runs, the volatile products were usually evolved within the first 2 hr. and remained essentially constant during the remaining time. The first species detected was CH_2Cl_2. Methylene chloride is tenaciously held by P-BEP and cannot be completely removed, even after several days of continuous pumping at 10^{-4} mm. The methylene chloride content of various samples does not appear to be related to how long the sample is pumped. In some cases, samples pumped for 2 hr. yielded about 1.0 to 1.5 ml. CH_2Cl_2 per gram of P-BEP, while samples pumped for several days yielded 2.5 to 3.0 ml. gas.

(C) After CH_2Cl_2 has been liberated, three primary volatile decomposition products from P-BEP are observed. These products are HF, HCN, and HNF_2. They all appear nearly simultaneously within the first few scans depending upon the temperature of the run. With increasing temperature, products were evolved more quickly and in greater concentration. However, even at the low temperatures and times, trace quantities may have been present.

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TABLE II

VOLATILE PRODUCTS EVOLVED FROM P-BEP AS A FUNCTION OF TEMPERATURE, TIME, AND METAL CONTAINER (C)

	Time (days)	T (°C)	CH_2Cl_2 (ml/g)	HF (ml/g)	HNF_2 (ml/g)	HCN (ml/g)	N_2O (ml/g)	Remarks
Copper	7	25	1.7	-	-	-	-	
"	19	25	-	-	-	-	-	
"	0.7	60	1.6	-	-	-	-	
"	0.7	77	2.0	-	-	0.2	-	
"	0.7	80	1.4	3	0.02	0.8	0.5	
"	0.7	80	3.0	9	0.02	1.0	1.3	
"	0.7	100	0.8	4	0.20	0.8	0.1	
"	0.7	110	1.7	12	-	0.7	1.0	
"	0.7	120	2.1	23	-	0.3	0.8	
"	0.3	130	0.8	7	0.02	1.1	0.6	
Monel	0.7	100	2.6	26	0.16	2.4	1.1	
"	0.7	100	2.6	34	0.40	3.5	3.0	
"	0.7	112	1.6	32	0.06	1.8	0.8	
Ni	0.7	100	2.2	29	0.10	2.7	0.7	
Stainless Steel	1	40	2.8	-	-	-	-	
"	4	40	2.8	-	-	-	-	
"	6	40	2.4	-	-	-	-	
"	0.7	50	0.4	-	-	-	-	
"	1	55	2.8	-	-	-	-	
"	4	55	3.0	tr*	0.01	0.3	0.2	
"	6	55	2.8	-	0.01	0.7	0.8	
"	0.7	60	2.3	-	0.03	0.4	-	
"	0.7	60	2.7	1	0.03	0.8	-	
"	0.7	60	0.7	-	-	0.1	-	
"	0.7	70	5	1	0.04	1.7	-	NF_3 (tr)
"	4	70	3.0	1	0.02	1.5	0.6	
"	6	70	3.0	1	-	0.7	2.1	
"	0.7	80	1.6	1	0.40	0.4	0.1	
"	0.7	80	2.1	1	0.02	0.9	1.0	
"	0.7	80	1.5	2	-	0.8	1.1	
"	0.7	80	2.3	1	-	0.6	0.8	
"	0.7	100	2.3	12	0.04	2.6	0.8	
"	0.7	100	1.9	23	0.10	2.2	0.8	
"	0.7	100	2.7	40	0.30	4.3	1.4	
"	0.7	100	1.9	11	0.10	2.4	0.2	

* Trace quantities

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(C) Infrared is not particularly sensitive to very small quantities of material. Our calibrations indicate the following limits of detection: HF - 1 ml/g; HCN - 0.1 ml/g; HNF_2 - 0.01 ml/g; N_2O - 0.1 ml/g; CH_2Cl_2 - 0.1 ml/g. These IR analyses were supplemented by GC and mass spectrometry which are somewhat more sensitive than infrared.

(C) Previous studies[7] have indicated that HCN and HNF_2 are generated from P-BEP in glass at ambient temperatures. The HF generated was found in very substantial quantities as SiF_4 which should be expected. It is not surprising that HCN is observed since many organo nitriles will liberate HCN at room temperature. It does indicate, however, that the P-BEP polymer does contain some nitrile functionalities.

(C) The fact that HF, HNF_2, and HCN are observed in the gas phase decomposition products seems to indicate that decomposition occurs through radicals F, NF_2, and CN. These radicals apparently abstract available H atoms from the polymer before they have a chance to react with themselves to form halogen or pseudo-halogen type molecules.

(C) The stable decomposition products, CO_2 and N_2O, are for most cases insignificant in the 16-hr. studies. These materials appear in large quantity only if substantial amounts of the primary products (HF, HNF_2, and HCN) are present.

(C) The amounts of gas evolved do not affect substantially the infrared spectrum of P-BEP residue. In most of the runs reported in Table II, smears of P-BEP residue were spread on AgCl plates and the infrared spectra recorded. In every case, no major change was detected in the solid residue when compared to a similar sample of unheated P-BEP. For example, no increases in the C≡N functionality or in the C=O functionality were detected. This observation leads us to believe that elimination of F, NF_2, and CN to form HF, HNF_2, and HCN is probably due to random extraction of hydrogen from the polymer.

(C) From the amounts of these primary products, it would appear that the most abundant decomposition radical is F; the next most abundant would be CN which forms HCN, and finally NF_2 which yields HNF_2. The evolution of HF, HCN, and HNF_2 is very rapid within the first few hours when heating P-BEP at a constant temperature. After these products are evolved the rate of evolution falls off rapidly and nearly ceases below 80°C. Above 80°C the same is noted except that the rate of product evolution

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[7] McElroy, A. D., and J. W. Nebgen, Midwest Research Institute, Report No. AFRPL-TR-67-304, December 1967, on Air Force Contract No. F04611-67-C-0022.

does not fall off as much. We interpret this observation to mean that the lower molecular weight fractions of P-BEP (which are generally assumed to be less stable than the higher fractions) are responsible for the degradation products noted in the infrared spectra. After these low-weight fractions are decomposed, degradation of the more stable, more abundant higher-weight fractions occurs at a very much slower rate at any given temperature.

(C) In addition to the overnight runs in which the volatilization of products was followed; a series of runs were made in which P-BEP polymer was heated and its spectrum recorded continuously overnight (16 hr.). The spectra show that little internal change occurred in the P-BEP over the temperature range studied (60°C to 140°C). This lack of change is in accord with the interpretation that the low molecular fragments of the P-BEP polymer decompose first. Early runs at 200°C indicated that pronounced changes occurred at elevated temperatures where $-C\equiv N$ functionalities readily appeared within a few hours.

(U) 3. <u>Gas chromatography</u>: A gas chromatographic (G.C.) analysis was made of gaseous products evolved in the overnight (16 hr.) P-BEP stability studies and on all the longer-term investigations. The technique enabled the identification and quantitative analysis of N_2, O_2, CO, NO, CO_2, and N_2O evolved as P-BEP decomposition products. The limit of sensitivity to the first four gases was approximately 0.02 ml. of gas/g of P-BEP while the CO_2 and N_2O could be quantized to 0.1 ml/g of P-BEP.

(U) Little gaseous decomposition was detected by G.C. in 16 hr. below 70°C. At 70°C only trace quantities of N_2, CO, NO, and CO_2 were detected. After longer time intervals decomposition products could be detected at lower temperatures. Table III shows the results of a number of the G.C. analyses. The quantities of decomposition products detected at 40, 55, and 70° after 6 days are shown in Figure 7.

(U) 4. <u>Electron spin resonance</u>: Electron spin resonance (ESR) studies were made to ascertain whether P-BEP contained residual paramagnetic species or whether such species could be detected during its thermal decomposition. An evacuated sample (40 - 50 mg.) was placed in the variable temperature assembly and spectra were obtained at temperatures from 25° to 175°C. No absorption peak was observed from 25° to 130°C. At 130°C a peak began to appear and increased in intensity with increasing temperature to 170°C. This is the same temperature region where changes could begin to be noted by infrared. Additional studies of the neat material at temperatures up to 200°C produced a moderate increase in the signal level, but no additional fine structure was resolved. Rapid cooling of the sample to -150°C did not show any appreciable improvement in the fine structure.

TABLE III

GAS CHROMATOGRAPHIC ANALYSES OF P-BEP DECOMPOSITION PRODUCTS (U)

Time (hr.)	Temp. (°C)	Gaseous Product (ml/g of P-BEP)				
		N_2	CO	NO	CO_2	N_2O
16	70	-	-	(t)*	(t)	-
16	80	0.3	0.1	0.04	0.2	0.2
16	100	0.3	0.1	-	0.2	(t)
24	40	-	-	-	-	-
24	55	-	-	-	-	-
96	40	0.1	-	-	(t)	-
96	55	0.2	0.05	-	(t)	-
96	70	0.5	0.2	-	0.2	(t)
144	40	-	-	-	(t)	-
144	55	0.5	0.1	-	0.5	0.3
144	70	1.6	0.5	-	1.7	0.8

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* Trace quantities are denoted by (t).
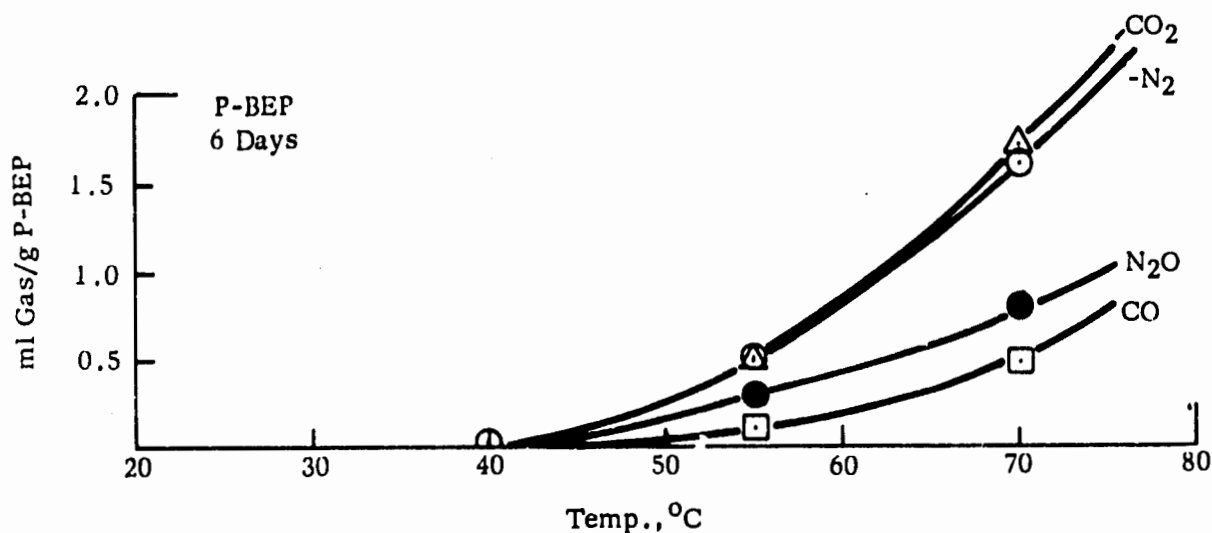
Figure 7 - Gaseous Products from P-BEP as a Function of Temperature

(U) Using the Varian computer of average transients (CAT) accessory, a time-average spectrum of 36 1-minute scans was obtained. It was of sufficient detail and intensity to show the observed signal to be a singlet having a g-value very close to 2.001 (Figure 8).
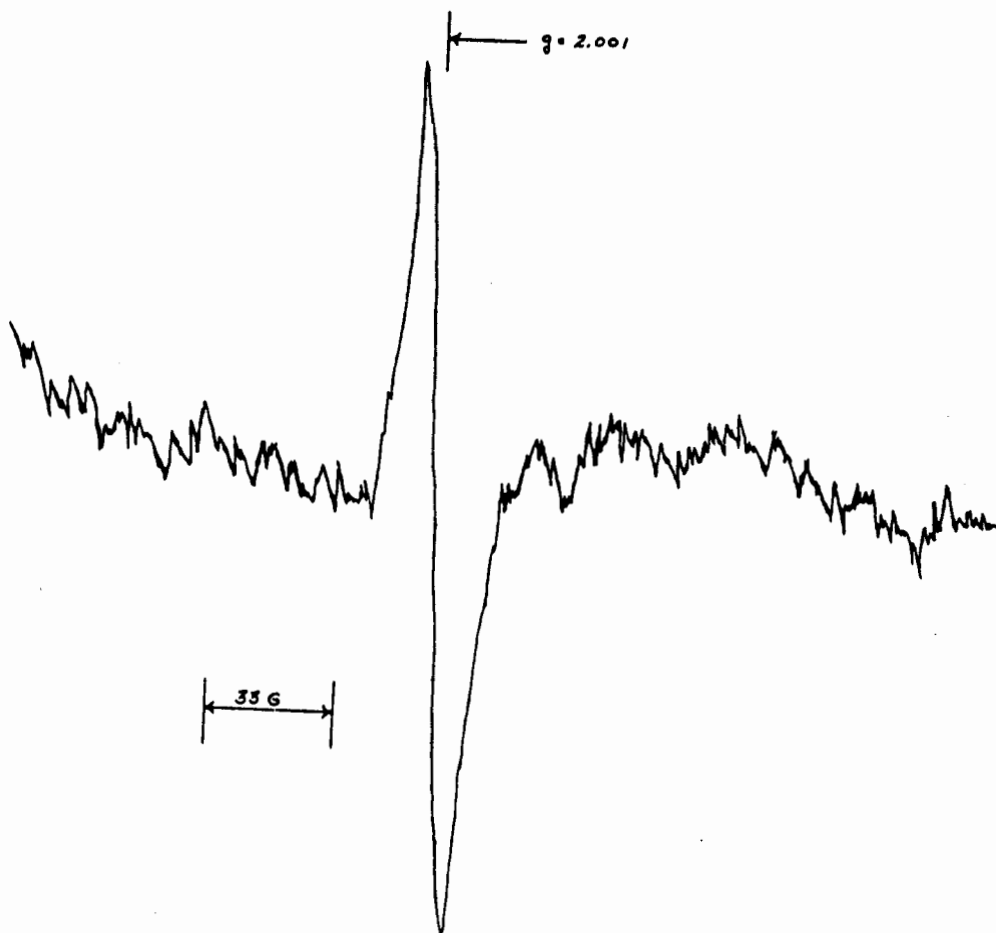
Figure 8 - Time Average EPR Spectrum of P-BEP
Absorption Peak

(C) The signal was sufficiently narrow that N, F or H splitting should have been resolved, were it present. Based on the assumption that the unpaired electron was located on an atom not bonded to any of the above three nuclei, only two bond cleavages could lead to such a radical. They are:

$$R\!\!-\!\!\left[\begin{array}{c} CH_2\text{-}NF_2 \\ O\text{-}C\text{-}CH_2 \\ NF_2 \end{array}\right]$$
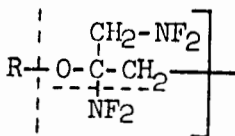
If a C-O bond cleavage were to occur, it would more likely occur adjacent to the tertiary carbon atom. As a consequence, it is likely that the signal is due to cleavage of the NF_2 group off of the tertiary carbon. It is not surprising that the companion NF_2 radical is not observed since it can not be detected by EPR in N_2F_4 under conditions where it is known to be present in appreciable concentrations.

(C) 5. <u>Nuclear magnetic resonance</u>: Nuclear magnetic resonance (NMR) studies were undertaken to determine if detectable changes in P-BEP occurred within the framework of temperatures previously discussed. Because of instrument temperature limitations and solvent volatility, NMR studies were restricted below 130°C. No significant changes in the ^{19}F or ^{1}H NMR spectra were noted. These observations substantiate IR studies of the solids as a function of temperature.

B. <u>P-BEP/Oxidizer Compatibility</u>

(C) 1. <u>Infrared studies</u>: Gaseous decomposition products evolved from P-BEP/oxidizer mixtures were investigated by infrared spectroscopy, gas chromatography and mass spectrometry. The primary objective was to determine the compatibility of HAP and HP-2 with P-BEP. Studies with AP were included for reference purposes.

(C) P-BEP/oxidizer systems were studied in the same manner as pure P-BEP. Oxidizers considered were HAP, HP-2 and AP. A 2:1 weight ratio of P-BEP to oxidizer was used in these studies (100 mg. to 50 mg. respectively). The infrared data are presented in Table IV. The numbers are reported in standard milliliters of gas evolved per gram of P-BEP.

(C) The infrared spectra indicate that considerably larger quantities of degradation products are noted in the P-BEP/HAP and P-BEP/HP-2 systems when compared to P-BEP alone. The P-BEP/AP system is changed little from that of pure P-BEP.

(C) Continuous generation of volatile decomposition products is noted, in contrast to the pure P-BEP where products were evolved early and reached a constant value. We also observed N_2F_4 as a P-BEP decomposition product when HAP and HP-2 were present and NF_3 occasionally. The evolution of N_2F_4 and NF_3 appears to relate to HNF_2 since HNF_2 occasionally disappears in the 16-hr. runs accompanied by increases in the quantities of N_2F_4.

(C) Another interesting observation is that CH_2Cl_2 reacts out of the system. In all of the long-term studies methylene chloride content in the gas phase is decreased substantially. At 55° and 70°C all CH_2Cl_2 is virtually reacted out. In pure P-BEP the long-term studies did not indicate so marked a decrease nor is it noted in the P-BEP/AP systems at long times.

TABLE IV

VOLATILE DECOMPOSITION PRODUCTS AS DETERMINED BY INFRARED
IN P-8EP/OXIDIZER SYSTEMS AS A FUNCTION
OF TEMPERATURE AND TIME (C)

Oxidizer	Time (days)	T (°C)	CH_2Cl_2 (ml/g)	HF (ml/g)	HNF_2 (ml/g)	HCN (ml/g)	H_2O (ml/g)	Remarks
HNF	7	25	1.1	-	-	-	-	
"	14	25	1.6	-	-	-	-	
"	18	25	0.8	..	-	-	-	
"	7	40	1.5	-	-	-	-	
"	16	40	1.6	tr*	0.03	0.6	-	
"	21	40	0.4	-	-	0.2	2.5	
"	0.7	55	2.7	-	-	-	-	
"	0.7	55	2.8	tr	0.04	0.8	tr	N_2F_4 (0.1)
"	7	55	1.5	-	-	1.1	1.0	N_2F_4 (2)
"	16	55	-	2	0.02	-	9.0	N_2F_4 (2)
"	21	55	-	2	-	1.6	4.1	N_2F_4 (4)
"	0.7	65	2.1	1	0.14	1.3	2.1	N_2F_4 (0.3)
"	0.7	65	2.1	9	0.23	2.5	1.8	N_2F_4 (0.5)
"	7	70	2.6	4	-	-	13.5	NF_3
"	14	70	-	2	-	0.9	20	Unidentified
"	18	70	-	4	-	-	20	NF_3
"	0.7	80	2.6	16	0.52	4.2	4.0	N_2F_4 (3)
"	0.7	80	2.8	8	0.07	3.5	4.4	
"	0.7	80	0.6	7	0.02	2.5	6.0	
"	2.5	85	2.2	14	-	-	8.4	
HP-2	4	25	2.2	-	0.01	0.3	0.2	
"	4	40	2.2	-	-	1.0	2.5	NF_3
"	0.7	50	2.2	-	tr	0.9	1.2	N_2F_4 (tr)
"	0.7	50	3.5	-	0.09	1.0	tr	
"	4	55	-	3	-	1.7	12.5	N_2F_4 (4), NF_3 + unidentified
"	0.7	60	0.7	-	0.16	1.0	-	
"	0.7	60	2.5	-	0.14	2.9	1.4	N_2F_4 (0.6)
"	4	70	-	-	-	-	20	NF_3
"	0.7	80	3.0	8	0.53	4.7	3.0	N_2F_4 (2)
"	0.7	80	1.2	7	0.11	3.3	4.7	N_2F_4 (0.2)
"	0.7	80	2.3	7	0.19	3.1	2.2	N_2F_4 (2)
"	1	85	0.6	3	-	1.7	6.4	
"	4	85	-	15	-	0.6	30	NF_3
AP	6	40	2.4	-	-	-	tr	
"	0.7	55	3.8	-	0.01	-	-	
"	6	55	2.8	-	0.02	0.7	0.8	
"	0.7	65	2.3	1	0.02	0.1	-	
"	6	70	2.8	tr	-	2.0	1.0	
"	0.7	80	4.0	2	0.05	0.8	tr	
"	0.7	80	1.1	1	0.03	0.3	-	

* Trace quantities

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(C) In general, it would appear that at high temperatures (above 60°C) both HAP and HP-2 greatly affect the P-BEP decomposition. Below 60°C, HAP appears to be substantially less reactive than HP-2. The change at 60°C in HAP is attributed to the crystal phase change (or possibly to dehydration) which occurs at that point in crystalline HAP. The high-temperature phase is less stable and would be expected to be more reactive. Our studies substantiate this greater reactivity.

(C) The P-BEP/AP system is very similar to P-BEP alone. The principal difference appears to be in the observation that the initial decomposition products (HF, HNF_2, and HCN) do not appear immediately as in the case of pure P-BEP but at some later time (5-10 hr.). As with pure P-BEP, these products increase in concentration very slowly with time.

(C) Of the three oxidizers considered here, AP is the most compatible with P-BEP; HAP is marginally compatible at temperatures below 60°C and HP-2 is the least compatible.

(C) 2. <u>P-BEP/HP-2 gas chromatography</u>: HP-2 was the most reactive of the three oxidizers with P-BEP. Significant amounts of reaction could be detected at 50°C in 16 hr. Gaseous products detected by G.C. at this temperature included N_2, CO, NO, CO_2 and N_2O. In longer-term studies the quantities of the gaseous products increased significantly even at 40°C. Large quantities of CO, CO_2, and N_2O were formed, indicating the oxidative degradation of P-BEP was occurring. It is not apparent whether N_2O was being formed by the oxidation of the hydrazinium ion or by attack of the NF_2 substituents on P-BEP. Nitrogen is a major gaseous product from the P-BEP/HP-2 reaction. Studies on the thermal decomposition of HP-2 at MRI[7] and at Reaction Motors Division of Thiokol Chemical Company[8] showed N_2 as a decomposition product but no evidence for the formation of N_2O. It appears, therefore, that N_2 formation is a measure of oxidizer degradation while the CO, CO_2, and N_2O are indicative of P-BEP degradation and/or oxidation. Figure 9 shows the quantities of gas evolved at 25, 40, 55 and 70°C in 4 days from a P-BEP/HP-2 mixture. By comparison the quantities of these gases evolved from P-BEP or HP-2 alone over this time period are two orders of magnitude smaller. For example, the total quantity of N_2, CO, CO_2, and N_2O evolved from P-BEP in 4 days is < 1 ml/g of P-BEP. At 70°C over the same time period < 0.1 ml. of gas/g is evolved from HP-2. This compares to over 100 ml. of gas evolved per gram of P-BEP or 200 ml/g of HP-2 evolved from the mixture. At 40°C little decomposition of either P-BEP or HP-2 can be detected in 4 days while the mixture liberates > 13 ml. of gas per gram of P-BEP.

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[8] Grelecki, C. J., and W. Cruice, Advances in Chemistry Series No. 54, p. 73 (1966).
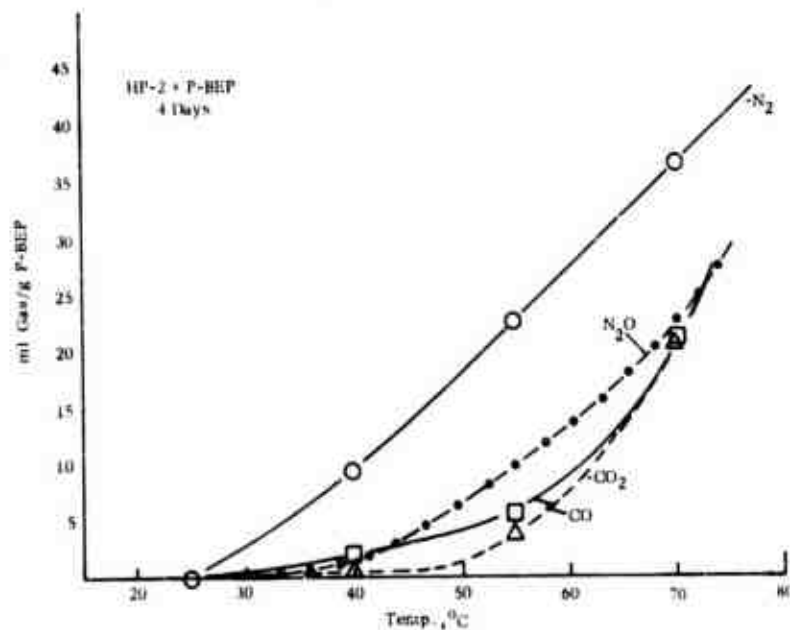
Figure 9 - P-BEP/HP-2 Decomposition Products Detected by Gas
Chromatography After 4 Days

(c) Assuming that the N_2 evolved is a measure of the degradation of HP-2,
the quantity detected corresponds to a 40-50 percent loss of oxidizer at
70°C in 4 days. The CO, CO_2, and N_2O detected indicate approximately a
10 percent decomposition of P-BEP. By comparison at 40°C a 15 percent
decomposition of HP-2 and < 1 percent decomposition of P-BEP is observed
in 4 days.

(c) P-BEP/HAP: The P-BEP/HAP mixture appeared to be less reactive than
P-BEP/HP-2, particularly below 55°C. The gaseous products observed by
G.C. were N_2, CO, NO, CO_2, and N_2O. Nitric oxide was often observed in
the 16-hr. studies but was seldom detected in longer-term studies. Figure 10
shows the quantities of gas evolved from a P-BEP/HAP mixture in 7 and
18 days at 25, 40, 55 and 70°C.

(c) The 16-hr. studies showed little reaction at 55°C or lower tempera-
tures. At 65°C and 80°C appreciable amounts of reaction were detected.
The results of the 16-hr. studies indicate that HAP is slightly more reac-
tive with P-BEP above 60°C than is HP-2; however, 4-day studies show the
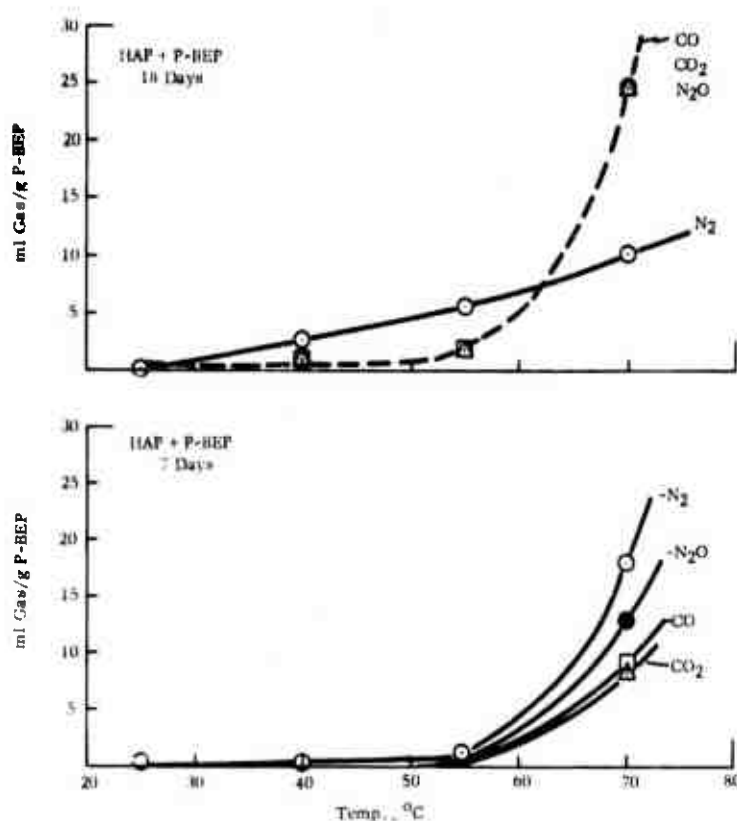reverse to be true.

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Figure 10 - P-BEP/HAP Decomposition Products Detected by Gas
Chromatography After 7 and 18 Days

(C) HAP is reported to undergo a crystal phase change at 60°C.[9] Recent
communications with personnel at NOS, Indian Head, Maryland,[10] indicate
that this change may instead be a dehydration of HAP. If HAP does dehydrate
at 60°C, the water liberated could promote decomposition leaving the impres-
sion that HAP is more reactive than HP-2 above 60°C. In longer-term stud-
ies, however, the relative amount of product formation promoted by the
water liberated would be small compared to the total amount of reaction
products generated and thus HP-2 over more extended time periods might
again prove to be more reactive. These results support this interpreta-
tion.

(C) <u>P-BEP/AP</u>: The P-BEP/AP mixtures show little if any reaction beyond
that expected for P-BEP alone. Figures 11 and 7 show the relative amounts
of gaseous products generated by the P-BEP/AP mixture and P-BEP alone.
These results indicate that, in fact, AP may have a stabilizing effect on
P-BEP.

9/ Dickens, B., Naval Ordnance Station, Indian Head, Maryland (to be
     published).
10/ Private Communications with Mr. Charles Cox at NOS, Indian Head, Maryland.
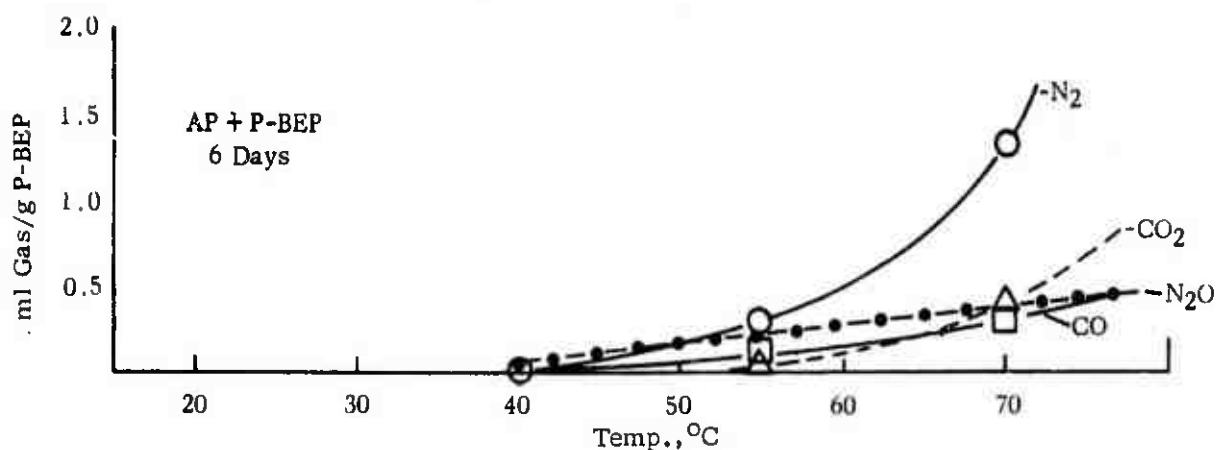
Figure 11 - P-BEP/AP Decomposition Product Detected by Gas Chromatography After 6 Days

C. P-BEP/Curing Agent Compatibility

(C) Preliminary studies involving the decomposition of P-BEP/curing agent systems have been undertaken using infrared techniques. Curing agents considered are DDI and ERLA-4221. Results are presented in Table V.

(C) The P-BEP/curing agent ratio was approximately 1:1 by weight. The materials were studied before the system cured. After heating for one day (or overnight) the product was a fairly hard solid in both cases.

(C) The P-BEP/DDI and P-BEP/ERLA-4221 systems gave about 10 percent of the quantities of products evolved from analogous pure P-BEP systems. These preliminary results seem to indicate that P-BEP is less susceptible to thermal degradation in a cured system than it is by itself. These studies are continuing to develop a more definitive picture of the P-BEP/curing agent compatibility.

TABLE V

VOLATILE DECOMPOSITION PRODUCTS AS DETERMINED BY INFRARED
FOR P-BEP/CURING AGENT SYSTEM AS A FUNCTION OF TEMPERATURE AND TIME (C)

Curing Agent	Time (days)	T (°C)	CH_2Cl_2 (ml/g)	HF (ml/g)	HNF_2 (ml/g)	HeN (ml/g)	N_2O (ml/g)	CO_2 (ml/g)
DDI	0.7	80	1.9	1	-	0.9	-	-
"	0.7	80	2.0	-	-	1.2	-	-
"	0.7	80	1.7	-	-	0.6	-	-
"	0.7	80	0.7	-	-	-	-	-
"	1	85	1.5	-	-	-	-	-
ERLA-4221	0.7	80	0.5	-	tr*	0.2	-	-
"	0.7	80	2.9	1	0.05	2.1	-	-
"	1	85	2.4	-	-	-	-	-

* Trace quantities

SUMMARY OF RESULTS

A. P-BEP Stability

(U) Chemical changes in neat P-BEP together with the identification and measurements of the rates of formation of gaseous decomposition products were studied to obtain a more definitive picture of the mode of P-BEP decomposition. The results of this investigation complement and supplement the findings of other investigators who have looked at P-BEP stability. The following conclusions regarding P-BEP stability can be drawn from this study.

(C) 1. It is extremely difficult to remove the last traces of methylene chloride from neat P-BEP. Vacuum stripping at 10^{-4} Torr and 50°C for 2 hr. will leave approximately 1 weight percent residual methylene chloride in the polymer.

(C) 2. P-BEP shipped in a methylene chloride solution contains small quantities of acetone and hydrocarbon impurities. These impurities can be removed by precipitating the P-BEP from methylene chloride with Freon-11. Trace quantities of Freon-11 are left in P-BEP purified by this procedure.

(C) 3. The principal low temperature gaseous decomposition products obtained from P-BEP are HF, HCN and HNF_2. The relative quantities of these gases, as detected by IR and direct inlet mass spectrometry, were $HF > HCN > HNF_2$. Methylene chloride appears to promote the formation of these gaseous products.

(C) 4. Hydrogen fluoride is liberated in small quantities at 25°C. P-BEP containing methylene chloride, when allowed to stand several days, contains more free HF than does P-BEP which has been stripped of methylene chloride.

(C) 5. The rate of HF evolution increases slowly as the temperature is raised from 30 to 70°C. A plot of the log (HF^+) versus $1/T$ gives a straight line over this temperature range. This line crosses the temperature intercept at 5°C, indicating that HF elimination below this temperature is negligible. The rate of HF elimination increases rapidly above 85°C which suggests a change in mechanism of HF elimination.

(C) 6. The rate of HCN elimination increases slowly up to 85°C. Above 85°C the rate increases significantly. A plot of log (m/e 27 intensity) versus $1/T$ indicates that HCN can be liberated at or below room temperature once dehydrofluorination to form the nitrile functionability has occurred.

(C) 7. Difluoramine begins to appear as a decomposition product in the infrared spectra at approximately 50°C and increases slightly with temperature. At 80-85°C the quantity of HNF_2 liberated increases more rapidly with temperature.

(U) 8. In the vicinity of 80-85°C P-BEP decomposition becomes very complex, liberating significant quantities of a variety of gaseous decomposition products.

(C) 9. CO, CO_2, NO, N_2O and N_2 are secondary products observed from P-BEP. These gases begin to appear in trace quantities at 40°C after 4 days. After 6 days at 55°C approximately 1.5 ml. of these gases per gram of P-BEP have been liberated; the total gas evolved including HF, HCN and CH_2Cl_2 was 5.0 ml/g of P-BEP. At 70°C the quantities of N_2, CO, CO_2 and N_2O evolved increase to a total of 3.6 ml/g of P-BEP in 6 days and the total gas evolved to 8.3 ml/g of P-BEP. A large portion of the total gas is CH_2Cl_2 ($\sim$ 2 ml/g of P-BEP).

(U) 10. Little chemical change was detected by IR in P-BEP polymer in 16 hr. below 130°C.

B. P-BEP/Oxidizer Compatibility

(C) The compatibility of P-BEP with AP, HAP and HP-2 was investigated.

(C) 1. Ammonium perchlorate is two orders of magnitude more compatible with P-BEP than either HAP or HP-2. It does not appear to promote the decomposition of P-BEP below 80°C and may in fact have a stabilizing affect. HF, HCN and HNF_2 are not liberated as quickly at 80°C in the P-BEP/AP mixture as from neat P-BEP.

(C) 2. P-BEP decomposition is accelerated appreciably by HAP and HP-2. Both oxidizers appear to promote C-N bond cleavage resulting in formation of N_2F_4 which is not observed as a P-BEP decomposition product in the absence of oxidizers.

(U) 3. Methylene chloride reacts out of the system in the presence of both HAP and HP-2.

(U) 4. HAP appears to be more reactive than HP-2 above 60°C in the 16-hr. studies.

(U) 5. HP-2 is significantly more reactive than HAP over the temperature range 25-70°C in time periods over 16 hr.

(C) 6. The end reaction products CO, CO_2, N_2, and N_2O are formed in much larger quantities in the presence of HAP or HP-2 than in the presence of AP.

(C) 7. Approximately 5 ml. of gas/g of P-BEP was evolved from the P-BEP/HAP mixture at 55°C in 7 days. This compares to 56 ml/g of P-BEP evolved at 70°C in 7 days. P-BEP alone evolved only 8.3 ml/g of P-BEP at 70°C in 6 days with CH_2Cl_2 accounting for 3 ml. of the gas.

(C) The P-BEP/HP-2 mixture generated approximately 48 ml. of gas/g of P-BEP at 55°C in 4 days and 100 ml/g of P-BEP at 70°C in 4 days.

(C) 8. These results indicate that a 3-5 percent decomposition of P-BEP will occur in the presence of HAP in 7 days at 70°C while at 55°C, 0.3 to 0.5 percent decomposition occurs over the same time interval.

(C) 9. Assuming that the N_2 observed in the P-BEP/HP-2 studies is coming primarily from HP-2, approximately 50 percent of the HP-2 and 9-10 percent of the P-BEP is decomposed in 4 days at 70°C. At 40°C, 10 percent of the HP-2 and 1 percent of the P-BEP decomposed in 4 days.

C. P-BEP/Curing Agent Compatibility

(C) Both DDI and ERLA-4221 appear to be reasonably compatible with P-BEP. Less gaseous reaction product is observed in the presence of the curing agents than when neat P-BEP is heated. We anticipate that DDI may react with HF and HNF_2 and studies of the effect of the P-BEP decomposition products on the curing agents is needed.

VI.

CONCLUSIONS

(C) The research performed on this program has the objective of providing information relevant to the use of P-BEP as a constituent of solid rocket propellants. What then is the significance of the results viewed in the context of the proposed application? The reader should bear in mind that P-BEP has not, in studies discussed in this report, been incorporated in a complete binder-oxidizer system. We rather have looked at P-BEP alone and in combination with specific second propellant ingredients. Furthermore, one should not forget that P-BEP is somewhat of an unknown in structure and purity, and consists of fractions varying in molecular weight. As a consequence, one should not generalize freely in interpretations of results.

A. P-BEP Stability

(C) If one considers the problem in the light of the behavior of P-BEP in the absence of other propellant ingredients, one concludes the following:

(C) 1. The rate of P-BEP decomposition increases appreciably in the temperature range of 80° to 110°C. Above 110°C its decomposition is quite rapid.

(C) 2. That stability of P-BEP is barely acceptable for processing in the 55° to 80°C range, and one should expect decomposition which may affect cure and which can reasonably be expected to adversely affect storage. We do not, in other words, recommend propellant formulation above 55°C.

(C) 3. That curing of a propellant grain can be expected to proceed reasonably well at temperatures up to about 55°C. However, a curing temperature of 40°C or lower is to be preferred.

(C) 4. That experience at ambient temperature is not reassuring from the standpoint of long-term propellant storability. The quantities of materials, (HF, HCN, HNF_2) evolved at or near 25°C are perhaps small enough that gassing will not be a problem. On the other hand, these gases cannot at this point be considered as inert; and side reactions, if they occur, will adversely affect storage life.

B. P-BEP/Oxidizer Compatibility

(C) 1. HAP/P-BEP: The HAP/P-BEP system must be classified as slowly reactive at ambient temperatures and up to about 55°C. This system is less stable than P-BEP by itself. The order of reactivity is consistent, however, with observations elsewhere that P-BEP-HAP systems are curable and at least short-term storable. Experience with propellant formulating is better than one predicts from the behavior of HAP/P-BEP. Both decomposition and oxidative degradation of P-BEP are promoted by HAP at 40°C and lower. These reactions are expected to be less extensive in less fluid (cured) systems. However, our experiences would appear to indicate that even in cured binders, P-BEP and HAP will react slowly under normal storage conditions.

(C) 2. HP-2/P-BEP: HP-2 is apparently too reactive to be formulated with a P-BEP binder. Large quantities of gas are evolved even at 40°C (104°F). HP-2 promotes decomposition as well as oxidative degradation of P-BEP. It or the P-BEP decomposition products react rapidly with any residual methylene chloride left in the P-BEP. These results indicate that it would be extremely difficult to cure a P-BEP/HP-2 propellant without extensive degradation of both the P-BEP and HP-2. The high rates of gas evolution would preclude even a relatively short storage life assuming it could be cured in the first place.

(C) 3. AP/P-BEP: Only AP, of the three oxidizers studied, appears to be compatible with P-BEP. Over the time intervals studied it does not promote decomposition or oxidative degradation of P-BEP up through 70°C. Although the differences are small, AP may in fact improve the stability of P-BEP. Studies are under way to determine whether these observations will hold over longer time intervals.

C. P-BEP/Curing Agent Compatibility

(C) Preliminary data indicate little reaction between P-BEP and either DDI or ERLA-4221. It appears however, that both of these curing agents would react with the HF and HNF_2 being liberated to destroy the functionalities necessary for cure. Studies are under way to determine whether these undesirable reactions do occur.

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APPENDIX

(c) GLOSSARY OF TERMS

P-BEP   Poly-bis-difluoraminopropylene oxide; Shell Development Company.

DDI   Diisocyanate of polymerized vegetable fatty acids; General Mills, Incorporated.

ERLA-4221   Alicyclic diepoxy acetate; Union Carbide Corporation.

AP   Ammonium perchlorate; G. F. Smith Chemical Company.

HAP   Hydroxylammonium perchlorate; Thiokol Chemical Corporation, Elkton, Maryland; 97 percent pure by titration for weak acid.

HP-2   Hydrazinium diperchlorate; Thiokol Chemical Corporation, Brigham City, Utah; 98.8 percent HP-2; 0.3 percent AP; 0.1 percent $HClO_4$; 0.8 percent unknown.

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Ivan C. Smith
John W. Nebgen
Thomas W. Lapp

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13. ABSTRACT

(C) The stability of P-BEP and its compatibility with HAP, HP-2, AP and curing agents have been studied.

(C) P-BEP slowly evolves HF, HCN, and HNF_2 at or near 25°C. Although the quantities of these gases evolved are small, they are sufficient to have an adverse effect on curing reactions, and will likely create problems in long-term storage.

(C) Both HAP and HP-2 promote decomposition and oxidative degradation of P-BEP. HP-2 appears to be too reactive to be formulated into a propellant which utilizes a P-BEP binder. The prospects of obtaining a storable propellant from the HAP-P-BEP system appears to be marginal. Of the oxidizers studied, only AP seems to be compatible with P-BEP.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Oxidizers						
Perchlorates						
Compatibility						
Stability						
Reaction Mechanisms						
P-BEP						
HAP						
HP-2						
Ammonium Perchlorate						
Solid Propellants						
Binders						